HOSTED BY
ELSEVIER
CrossMark
Available online at www.sciencedirect.com
ScienceDirect
Biosurface and Biotribology 1 (2015) 130–134
www.elsevier.com/locate/bsbt

Nanocrystalline layer on the bearing surfaces of artificial hip implants induced by biotribocorrosion processes

Z.W. Wang, Y. Yan*, L.J. Qiao

Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, China

Received 12 March 2015; received in revised form 8 April 2015; accepted 20 May 2015

Abstract

Orthopedic prostheses are lubricated by a pseudosynovial fluid that contains proteins. Under regular movements, bearing surfaces would suffer wear and corrosion. More importantly, their interaction controls the material degradation process. Nanocrystalline layer was found on the surface of CoCrMo alloy surface after tribocorrosion tests. Tribocorrosion tests were taken in 0.9% NaCl and 0.9% NaCl with 1% bovine serum albumin (BSA) solution. Small angle X-ray Scattering was applied to measure the size distribution of the nano-crystals. As a general conclusion, proteins can absorb on prosthesis materials and act as a lubricant during sliding. The negative charge distribution on the material surface can promote the adsorption of protein. The average size of the nano-crystals on the bearing surface was 5 nm.

Keywords: Wear; Corrosion; Protein adsorption; SAXS

1. Introduction

In recent years, total hip replacements have obtained great attraction in research field as an effective treatment for millions of patients worldwide. CoCrMo alloys have become one of the most used metals for total joint replacements due to its appropriate hardness and elastic modulus. Research has been done to analyze the reasons of loosening for both of metal-on-metal and metal-on-polyethylene total hip replacements [1,2]. For metal-on-metal (MoM) joints [3,4], wear debris and released toxic ions have become main causes of failure. Pseudocyst caused by nano-sized debris was found during the use of CoCrMo alloy prosthesis [5]. In the previous studies [6–9], the effect of albumin, the major synovial protein, on the tribological behavior of the prosthesis materials was investigated, which has drawn a conclusion that the adsorption of proteins can interpret the differences in the friction behavior of different materials. The microstructure of the joint surface would have some unusual changes when compared in the normal environment and was considered as a key factor in the wear of MoM joints. This study aims to analyze the effect of surface potential on the protein adsorption on CoCrMo alloy. Small angle X-Ray Scattering was used to compare the size of nano-crystals under different conditions.

2. Materials and methods

2.1. Wear test

The main material used in the experiment was a CoCrMo alloy, the composition of which is listed in Table 1. Ultra-high molecular weight polyethylene was chosen as the counterpart. The diameter of the UHMWPE pin was 5 mm. The sliding wear tests were carried with a UMT-II friction wear tester. The coefficient of friction was recorded during sliding. The test parameters were set as follows: the average speed of sliding: 30 mm/s; the frequency of sliding: 1 Hz; the applied load was 5 N (corresponding to a nominal contact pressure of 200 MPa) and the longest sliding time was 8 h. 0.9% NaCl and 0.9% NaCl + 1% bovine serum albumin (BSA) solution were used as lubrication medium.

*Corresponding author.
E-mail address: yanyu@ustb.edu.cn (Y. Yan).

http://dx.doi.org/10.1016/j.bsbt.2015.05.001

Table 1
The chemical composition of the materials in this study (wt/%).

Materials	Co	Cr	Mo
CoCrMo alloy	Bal.	28	5

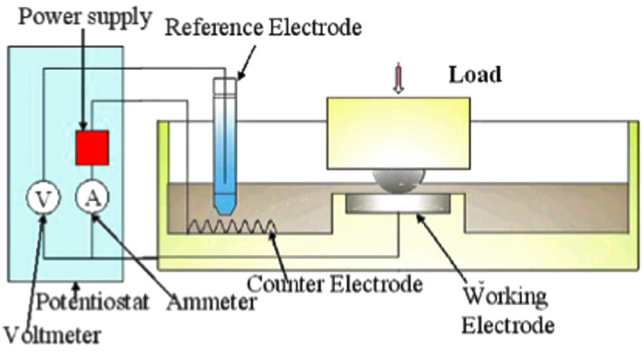

Fig. 1. Schematic representation of the integrated three-electrode cell.

The three-electrode electrochemical cell was used, in which the specimen acted as working electrode(WE), a platinum wire as the counter electrode(CE) and a silver/silver chloride electrode as the reference electrode(RE). Fig. 1 shows the integrated tribocorrosion tester so that the tribological and electrochemical data can be obtained synchronously.

2.2. Scanning electron microscopy (SEM)

SEM experiments were carried out with a ZEISS EV018 special edition microscope. Backscattered electron imaging mode was used to analyze the surface components of the CoCrMo alloy under different conditions.

2.3. Small Angle X-ray scattering(SAXS)

SAXS was used to determine the size, shape, and distribution of the nano-sized crystals in the wear track in different solutions and different conditions (at open circuit and under cathodic protection). The experiment was carried out at BRSF small-angle scattering station in the Institute of High Energy Physics, Chinese Academy of Sciences, 1W2A beamline. The storage ring of electronic energy was 2.5 GeV and the average beam intensity was 60 mA. The wavelength of the X-Ray used was 0.153 nm. The synchrotron radiation beamlines from electron–positron collider storage ring was focused and collimated before it irradiate on the specimen. The two-dimensional imaging plate(IP) CCD detector (Mar 165) was used to detect the changes of the light intensity with the scatter angle. The image pixels were 2048 × 2048, with each pixel 79 μm. The distance from the specimen to the detector was 1.58 m [10].

The specimens were removed directly after tribological tests. Table 2 shows the tribological conditions in SAXS experiment.

Table 2
The tribological conditions in SAXS experiments.

Specimen number	Lubricant	Applied potential	Time (h)
1	0.9% NaCl	OCP	8
2	0.9% NaCl	CP(−0.8 V)	8
3	0.9% NaCl+1%BSA	OCP	8
4	0.9% NaCl+1%BSA	CP(−0.8 V)	8
5 (Blank)	–	–	–

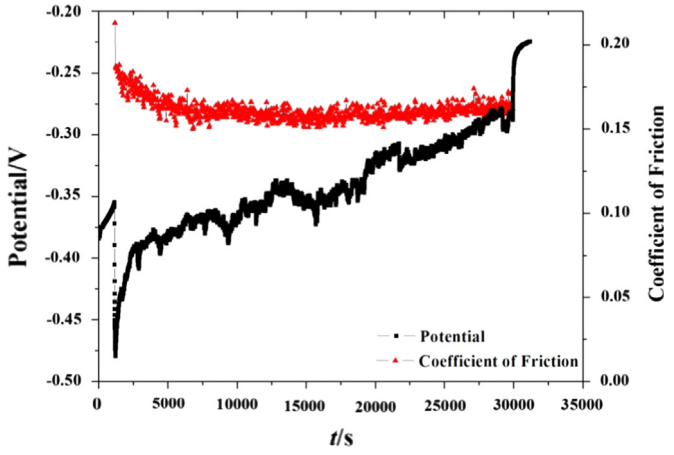

Fig. 2. Open circuit potential change vs. time for CoCrMo alloy in 0.9% NaCl solution.

3. Results and discussion

3.1. Open circuit potential(OCP) and cathodic protection(CP) measurements

A passive film can form on the surface of the material spontaneously. During sliding, this passive film was removed and then re-established. The shift of the open circuit potential with time can depict this process. Fig. 2 shows the coefficient of friction and the OCP during sliding for CoCrMo alloy disk and UHMWPE pin in 0.9% NaCl solution. When the load was added on the material, a shift was seen on the potential curve, which indicates that the passive film was removed and the metal surface was in an active status. And after 8 h sliding, the load was removed and the passive film was rebuilt on the metal surface, which caused a positive shift of the potential. There was a dynamic equilibrium of the removal and the re-establishment of the passive film during sliding, the relative velocity of the two procedures determined the value of the open circuit potential. A constant positive shift can be seen during sliding, indicated that the velocity of the re-establishment process was faster than the removal of the passive film.

Fig. 3 shows SEM images of CoCrMo alloy samples tested in different solutions and potentials. The dark region indicated the aggregation of light elements such as C, S, O, etc., which are the elements that protein contains. Protein adsorption can be observed on the surface of the samples sliding in protein environments (Fig. 3(a)), which is different from the sample sliding in 0.9% NaCl solution. The adsorption of proteins is

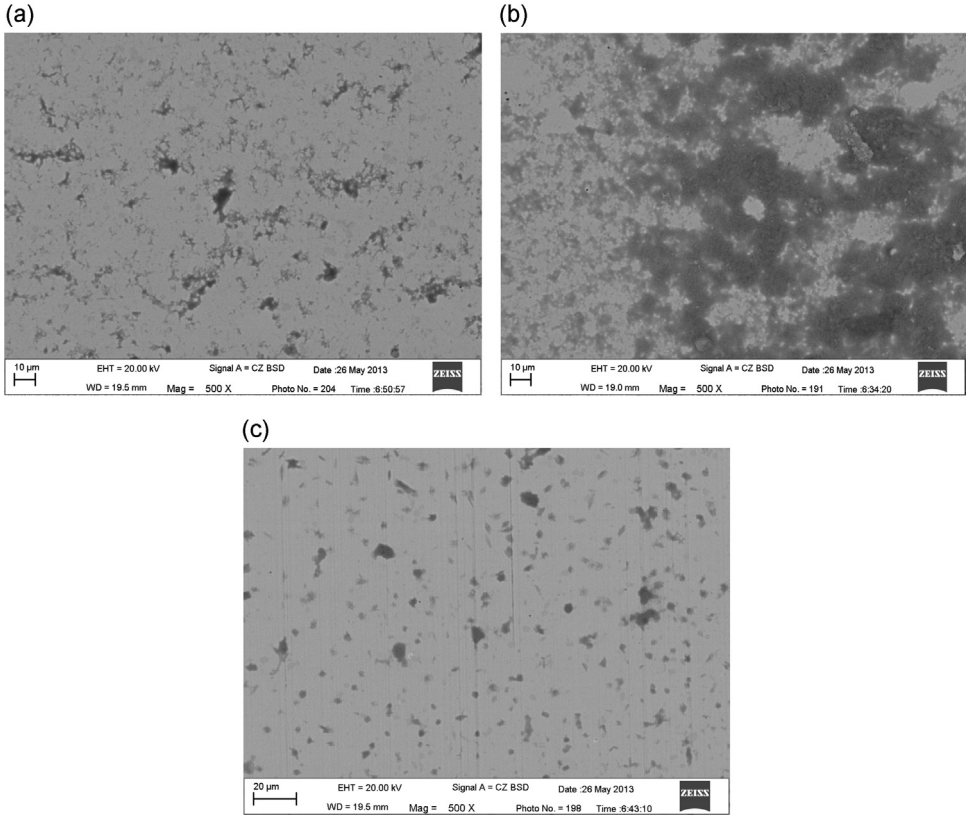

Fig. 3. Backscattered electron images of CoCrMo alloy in 0.9% NaCl+1% BSA solution after 8 h tribocorrosion tests with different potential: (a) OCP, (b) −0.8 V and (c) +0.2 V.

related to the type of protein and the properties of the material surface, including the distribution of charge, surface topography, surface energy and so on [11]. When a certain potential was applied on the surface of the material, the charge distribution of the material surface was changed, and thus it could affect the amount of adsorbed protein. There were more proteins adsorbed on the surface when a −0.8 V vs. Ag/AgCl potential was applied on the surface (Fig. 3(b)). With the positive shift of the applied potential, there were less proteins adsorbed on the surface (Fig. 3(c)). When a positive potential (+0.2 V vs. Ag/AgCl) was applied on the surface of the material, the surface was positively charged. As the charges on the surface and the protein were the same, so a weakened protein adsorption was observed.

A nanocrystalline (NC) layer was formed and the grain size was smaller than 100 nm for a tested bearing surface. This layer could be formed by the steady high strain field directly under the worn surface which brings about a constant sequence of deformation and recrystallization. And another possible process that may occur within the NC layer is the strain-induced phase transformation. The severely deformed alloy surface has been subjected to high strain levels and could transform from the meta-stable FCC structure in to an HCP phase. From Fig. 4(a), there is a lot of orientated ε-martensite lamellae appeared under the NC layer (about 500 nm from surface). And the stacking faults and twins can also be found in Fig. 4(a). The formation of twin structure and martensite depends on the slip of stacking fault for nucleating and extending. Due to the low stacking fault energy, CoCrMo alloy with FCC structure could easily generate that phenomenon. On the sliding planes, the martensite needles and stacking faults could react with each other and form the depicted triangular or rhombic cells with a size ranging from 10 to 100 nm. These cells may shear with each other by the high cyclic shear stress and form smaller grain size. Only the FCC structure of the substrate was found. And it is worth to note that there are some light lines appeared and connected the diffraction spot.

The appearance of diffraction rings testifies the existence of nanocrystal and the ring 1, 2 and 3 are all HCP structure and the orientation of these nanocrystals is unordered. But the film still contains crystal with FCC structure. The SAED results testify the transformation from FCC structure to HCP structure with the acting of strain. Nanocrystals were probably produced by shearing of cells generated by stacking faults and ε-martensite needles and moving toward the surface with the increasing of the strain gradient. The center of the diffraction is surrounded by a halo, and the halo may be produced by amorphous in the film (Fig. 5 (c)). These complexes may be mixed with the top surface and the absorbed protein by the stain and finally formed the film.

3.2. SAXS

The distribution of the size of the nano-crystals in the wear track can be described by the normal distribution theory [12]. Fig. 5 shows the size distribution after the revision of the positively deviated Porod curves. When the test was conducted under CP condition, the proportion of the nano-sized crystals

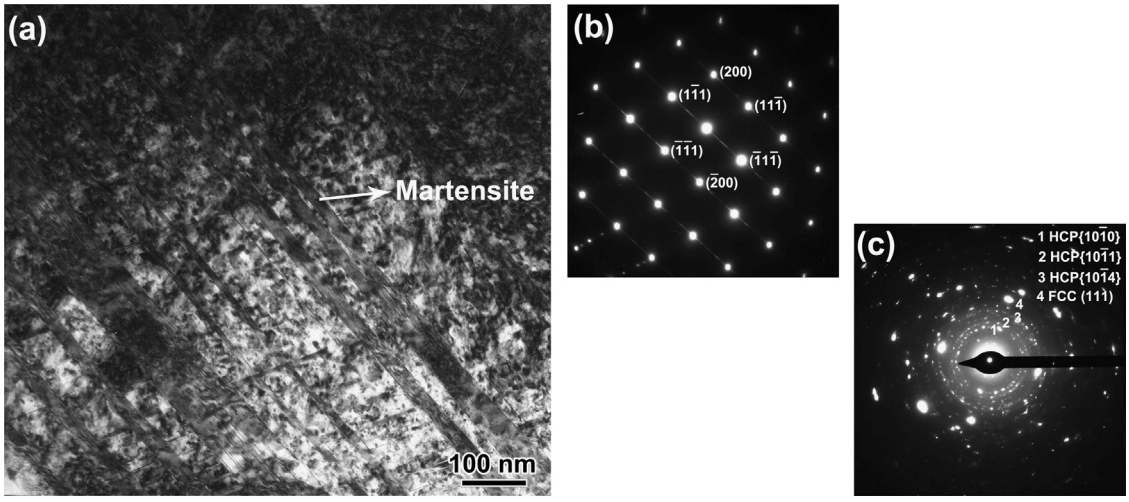

Fig. 4. (a) Light-field TEM image of the area under the NC layer (deep about 500 nm from surface), (b) and (c) the SAED of different areas.

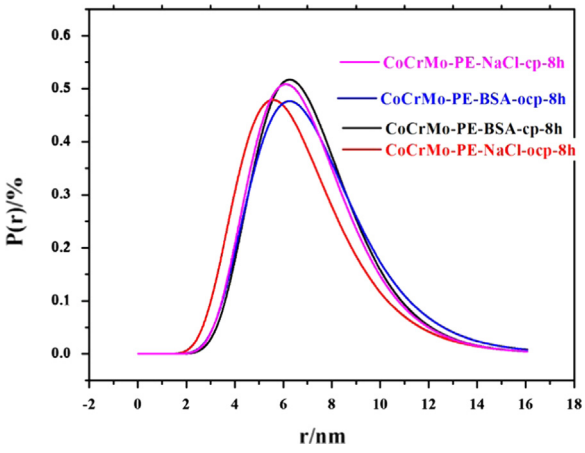

Fig. 5. The logarithmic distribution curve of the nano-crystals on the sample surface under different test conditions.

was more than that in OCP condition. As the negatively charged surface could enhance the adsorption of the protein, it may lead to the reduction of the amount of the nano-crystals induced by the mechanical–electrochemical synergy effect. With the existence of protein, the nano-sized crystals were larger than that produced in 0.9% NaCl solution, which demonstrated that the protein can inhibit the produce of the nano-crystals to some extent. However, the difference in the size of the nano-crystals under different conditions was really small. It indicates that the mechanical effect was the major reason for the formation of nano-crystals.

4. Conclusions

Wear tests with electrochemical setup were carried out to determine the effect of potential on the tribocorrosion process. SEM and SAXS analysis were conducted to have a better understanding of the formation of the protein film and the nanocrystalline layer on the bearing surface. Some conclusions can be drawn.

(1) The amount adsorbed proteins is related with the properties of the material surface. The negatively charged material can enhance the adsorption amount of the protein.
(2) The size and distribution of the nano-crystals in the wear track were measured by SAXS. The results show that the size of nano-crystals was similar in all tested conditions. It indicates that the formation of nanocrystalline layer was induced mainly by the mechanical force applied on the surface.

Acknowledgments

The authors would want to thank the support from the National Natural Science Foundation of China under Grand no. 51201011 and the Specialized Research Fund for the Doctoral Program of Higher Education 20110006120024.

References

[1] Christopher A. Zahiri, Thomas P. Schmalzried, Edward Ebramzadeh, Edward S. Szuszczewicz, David Salib, Carrie Kim, Harlan C. Amstutz, Lessons learned from loosening of the McKee-Farrar metal-on-metal total hip replacement, J. Arthroplast. 14 (1999) 326–332.
[2] K. Djef, O. Wahlstrom, S. Hammerby, Loosening 5 years after total hip replacement: a radiological study of the McKee-Farrar and Charnley prostheses, Arch. Orthop. Trauma Surg. 105 (1986) 339–342.
[3] A.C. August, C.H. Aldam, P.B. Pynsent, The Mckee-Farrar hip arthroplasty, J. Bone Jt. Surg. 68-B (1986) 520–527.
[4] F. Higuchi, A. Inoue, M. Semlitsch, Metal-on-metal CoCrMo McKee-Farrar total hip arthroplasty: characteristics from a long-term follow-up study, Arch. Orthop. Trauma Surg. 116 (1997) 121–124.
[5] R. Pourzal, I. Catelas, R. Theissmann, C. Kaddick, A. Fischer, Characterization of wear particles generated from CoCrMo alloy under sliding wear conditons, Wear 271 (2011) 1658–1666.
[6] A.P. Serro, M.P. Gispert, M.C.L. Martins, P. Brogueira, R. Colaco, B. Saramago, Adsorption of albumin on prosthetic materials: implication for tribological behavior, J. Biomed. Mater. Res.: A 78 (2006) 581–589.
[7] Jingyun Fan, Connor Myant, Richard Underwood, Philippa Cann, Synovial fluid lubrication of artificial joints: protein film formation and compositon, Faraday Discuss 156 (2012) 69–85.

[8] K.S. Kanaga Karuppiah, Sriram Sundararajan, Zhi-Hui Xu, Xiaodong Li, The effect of protein adsorption on the friction behavior of ultra-high molecular weight polyethylene, Tribol. Lett. 22 (2) (2006).
[9] R.L. Williams, D.F. Williams, Albumin adsorption on metal surfaces, Biomaterials 9 (1998) 206–212.
[10] I. Zizak, P. Roschger, O. Paris, et al., Characteristics of mineral particles in the human bone/cartilage interface, J. Struct. Biol. 141 (2003) 208–217.
[11] C.A. Haynes, W. Norde, Globular proteins at solid/liquid interfaces, Colloid Surf. B Biointerface 2 (1994) 517–566.
[12] D.M. Tiede, K.L. Mardis, Xiaobing Zuo, X-ray scattering combined with coordinate-based analyses for applications in natural and artificial photosynthesis, Photosynth. Res. 102 (2009) 267–269.